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Abstract

Background: Use of engineered nanoparticles (NPs) in consumer products is resulting in NPs entering drinking water sources. Subsequent NP breakthrough into treated drinking water is a potential exposure route and human health threat.

Objectives: This study investigated the breakthrough of common NPs, silver, titanium dioxide (TiO_2), and zinc oxide (ZnO), into finished drinking water following conventional and advanced treatment.

Methods: NPs were spiked into five experimental waters: groundwater, surface water, synthetic freshwater, synthetic freshwater with natural organic matter, and tertiary wastewater effluent. Bench scale coagulation/flocculation/sedimentation simulated conventional treatment, and microfiltration (MF) and ultrafiltration (UF) simulated advanced treatment. Breakthrough of NPs into treated water was monitored by turbidity removal and inductively coupled plasma – mass spectrometry (ICP-MS).

Results: Conventional treatment resulted in 2-20%, 3-8%, and 48-99% of silver, TiO_2, and ZnO NPs or their dissolved ions remaining in finished water, respectively. Breakthrough following MF was 1-45% for silver, 0-44% for TiO_2, and 36-83% for ZnO. With UF, NP breakthrough was 0-2%, 0-4%, and 2-96% for silver, TiO_2, and ZnO, respectively. Variability was dependent on NP stability with less breakthrough of aggregated NPs compared to stable NPs and dissolved NP ions.

Conclusions: Although a majority of aggregated or stable NPs were removed by simulated conventional and advanced treatment, NP metals were detectable in finished water. As environmental NP concentrations increase, we need to consider NPs as emerging drinking water

contaminants, and determine appropriate drinking water treatment processes to fully remove NPs

in an effort to reduce their potential harmful health outcomes.

Introduction

Engineered nanoparticles (NPs) are currently used in over 1200 commercially available consumer products, including personal care products, food storage containers, cleaning supplies, bandages, clothing, and washing machines (Reijnders 2006). These products release NPs into the domestic waste stream during use, cleaning, and disposal, leading to NPs in surface waters (Benn and Westerhoff 2008; Blaser et al. 2008; Mueller and Nowack 2008). Estimated concentrations of NPs in U.S. surface waters range up to 10 µg/L silver (Ag), 24.5 µg/L titanium dioxide (TiO_2) and 74 µg/L zinc oxide (ZnO) NPs (Blaser et al. 2008; Gottschalk et al. 2009; Mueller and Nowack 2008). Concentrations in surface water are anticipated to increase over time with greater use and disposal of NP-containing products (Klaine et al. 2008).

As NP concentrations increase in surface waters, it is important to consider the ultimate fate of NPs. When suspended in the water column, NPs are likely to affect aquatic organisms (Handy et al. 2008) and be present in surface waters used as source water for drinking water treatment plants. Environmental fate and transport of NPs are largely related to NP dissolution (Elzey and Grassian 2009) and aggregation of single NPs into larger agglomerates, which are more likely to settle out of suspension (Petosa et al. 2010). The extent of aggregation, final NP size, and interaction with natural organic matter (NOM) will impact the efficiency of NP removal during drinking water treatment (Hyung and Kim 2009; Zhang et al. 2008).

Water treatment is one of the main strategies to prevent the ingestion of harmful contaminants, including NPs, from drinking water (Hyung and Kim 2009). Conventional drinking water treatment typically involves coagulation, flocculation, and sedimentation. During coagulation, a

chemical, such as alum, is added to destabilize dissolved particles (EPA 1999). Destabilized particles aggregate into larger flocs during flocculation, which can then be removed by gravity sedimentation (Crittenden et al. 2005). To monitor effective drinking water treatment for NOM removal, the U.S. Environmental Protection Agency (EPA) has set guidelines on the required total organic carbon (TOC) removal by coagulation based on initial TOC and alkalinity (Supplemental Material, Table S1) (EPA 1999). Water treatment plants use turbidity and TOC as surrogate measures for NOM and contaminant removal.

In addition to conventional treatment, the use of low pressure membrane (LPM) filtration as an advanced water treatment technology has increased in prevalence over the past two decades (Huang et al. 2009). Unlike conventional treatment, LPM filtration relies on physical sieving to remove particulate contaminants (Crittenden et al. 2005). Therefore, the pore size of membranes employed in LPM filtration is expected to affect the removal of NPs in water.

Removal of NPs through drinking water treatment is not well understood. TiO_2 and ZnO NPs spiked into buffered ultra-pure and tap water achieved over 60% removal using alum coagulation and sedimentation (Zhang et al. 2008). Using carbon fullerene NPs (nC_{60}) spiked into synthetic freshwater, NP removal by simulated conventional treatment was correlated with NOM concentration (Hyung and Kim 2009). However, these studies did not test NP removal in natural waters with complex chemistries that can affect NP aggregation, dissolution, and removal. Additionally, in these studies, metal oxide NP removal was determined using graphite furnace atomic absorption spectroscopy with sensitivities in the mg/L range (Zhang et al. 2008). Use of more sensitive instrumentation, such as inductively coupled plasma – mass spectrometry (ICP-MS) with sensitivity in the ng/L range, is necessary to accurately assess NP and metal ion

removal from drinking water. The lack of accurate detection of NPs in finished drinking water has limited our understanding of NP exposure via drinking water.

The ingestion of NPs via drinking water may pose a potential direct human health threat or an indirect risk due to release of metal ions from the NPs. Metal NP or NP ion exposure via the ingestion can result in adverse effects including kidney damage, increased blood pressure, gastrointestinal inflammation, neurological damage, and cancer (EPA 2011; Kavcar et al. 2009; Vahter et al. 2002). Following *in vitro* NP exposure, researchers have shown cell uptake, cytotoxicity, and DNA damage in the Caco-2 human intestinal cell line (Abbott Chalew and Schwab 2013; Gaiser et al. 2012; Gerloff et al. 2009; Gerloff et al. 2012; Koeneman et al. 2010).

Exposure to NPs via the ingestion of drinking water has been tested using *in vivo* animal studies and revealed adverse effects. Rats and mice ingesting metal NPs had increased metal concentrations in their liver, kidneys, brain, and blood compared to controls (Kim et al. 2008; Park et al. 2010; Wang et al. 2007). Exposure to Ag and ZnO NPs in drinking water was found to cause histological evidence of inflammation as well as increased liver enzymes related to necrosis and inflammation in rats and mice (Cha et al. 2008; Park et al. 2010). Additionally, the ingestion of metal NPs was found to lead to DNA damage (Sharma et al. 2012; Trouiller et al. 2009). The consequences of increased metal burdens, DNA damage, and liver toxicity are not fully understood. However, these studies indicate that the ingestion of NPs can lead to NPs or metal ions in systemic circulation with potentially adverse consequences.

The objectives of this study were to investigate the removal of NPs during conventional and advanced water treatment, determine the effects of NP and water properties on the removal process, and investigate the magnitude of NPs and released ions not removed by the treatment

processes ("breakthrough"). The experiments were conducted using Ag, TiO$_2$, and ZnO NPs commonly present in consumer products that are also likely to be present in water. These NPs were also chosen to replicate previous studies and to represent potential environmental fate of NPs: stabilized as individual particles (Ag NPs), aggregation to larger aggregates (TiO$_2$ NPs), and dissolution into metal ions (Ag and ZnO NPs). Removal from groundwater, surface water, synthetic water with and without NOM, and tertiary wastewater effluent were investigated. Jar tests to simulate conventional treatment (coagulation/flocculation/sedimentation) and LPM filtration to simulate advanced water treatment. The removal of NPs was evaluated by traditional water quality parameters such as turbidity removal, TOC removal, and ultra-violet/visible light absorbance. In addition, ICP-MS was utilized for advanced quantification to further elucidate removal.

Materials and Methods

Nanoparticles. Ag, TiO$_2$ (Aeroxide P25), and ZnO NPs were purchased from Sky Spring Nanomaterials, Inc. (Houston, TX), Evonik Degussa (Pasippany, NJ) and NanoAmor (Houston, TX), respectively. The size and shape of NPs were determined by transmission electron microscopy (Phillips EM 420, Amsterdam, Netherlands). All particles were spherical or semi-spherical with average NP sizes at 83.6 nm, 33.7 nm, and 35.6 nm for Ag, TiO$_2$, and ZnO NPs, respectively (Supplemental Material, Figure S1).

Stock NP suspensions of 100 mg/L were prepared by weighing NPs on a Mettler Toledo microbalance (0.1µg sensitivity) (Columbia, MD), transferring weighed NPs into 15ml polypropylene tubes and subsequently adding sufficient ultra-pure water (Millipore, Billerica, MA) to achieve 100 mg/L. The suspension was vortexed for 10 seconds and pulse sonicated at

20 kHz for 4 minutes with 0.5 second pulses using a 550 Sonic Dismembrator (Fisher Scientific, Pittsburgh, PA). Suspensions were stored at room temperature for up to one week and resonicated before each experiment.

Water characterization. Five test waters were selected for NP removal experiments: a Maryland groundwater source (GW) currently used as drinking water, a suburban surface water source (SW) from central Maryland, synthetic freshwater (SFW) with and without NOM, and tertiary wastewater effluent (WWeff) from Maryland. The SFW was prepared with 50 mg/L $NaHCO_3$, 30 mg/L $CaSO_4$, 30 mg/L $MgSO_4$, and 2 mg/L KCl (all Optima grade reagents, Fisher Scientific). The NOM source for SFW_NOM was from water collected from the Great Dismal Swamp National Wildlife Refuge in southeastern Virginia (Huang and O'Melia 2008) and was diluted into SFW to a final concentration of 5 mg C/L (denoted "SFW_NOM") (for NOM characterization, see Supplemental Material, Table S2). Water samples were pre-filtered using 1.2μm glass fiber filters (Whatman GF/C) and stored at 4 °C. Waters were fully characterized (Supplemental Material, Table S3).

Characterization of nanoparticles in water. Using stock suspensions, NPs were diluted 1:10 into test waters and characterized for size (Table 1). Characterization was conducted at 10 mg/L to remain within the sensitivity range of the analytical instruments. Dynamic light scattering (DLS) using a Zetasizer ZS90 (Malvern Instruments, Westborough, MA) characterized NP size. The z-average values were reported as the mean of three samples of each NP in each water type with four measurements of 10 runs of 10 seconds each. Measurements were rejected if the count rate was below 100 kilocounts and the polydispersal index was above 0.7.

Metals analysis. Determination of NP removal was conducted by measuring total metal content by ICP-MS (Agilent, Santa Clara, CA), which was used as a surrogate for NP. A 300 µL aliquot of sample was combined with 700 µL of concentrated HNO_3 (Optima grade, Fisher Scientific) in 7 mL Teflon vessels and subsequently microwaved (CEM, Matthews, NC) using a program that raised the temperature to 165°C over 20 minutes, 175°C over an additional 7 minutes, and held at 175°C for 30 minutes. Samples were diluted with ultra-pure water to 2% HNO_3. In addition, HCl (Optima grade, Fisher Scientific) was added to reach 0.5% and 50 ppb of indium and scandium (Agilent, Santa Clara, CA) were added as an internal standard.

Output from the ICP-MS was converted into a mass per unit volume value, which was blank corrected using an ultra-pure water as a method blank. Unspiked waters were also digested to obtain background metal contamination levels in the waters which was used to background correct for each experimental water. Untreated 1 mg/L NPs in ultra-pure water, served as the reference material (RM) was prepared for each experiment and processed along with the samples. The limits of detection (LOD) were 3.95, 0.35, and 0.16 µg/L for silver, titanium, and zinc, respectively. If total metal concentrations in the samples were below the LOD, they were substituted with a value of half the LOD for statistical analysis.

Jar tests. Jar tests using a Phipps & Birds programmable jar tester (Richmond, VA) were conducted to determine the optimal coagulant dose. Test waters were spiked with 1 mg/L NPs from stock suspensions and mixed overnight by a magnetic stir bar at 60 rpm. Reagent-grade aluminum potassium sulfate ($KAl(SO_4)_2 \cdot 12H_2O$) (i.e. potassium alum) was dissolved in ultrapure water for a 2.8 g Al/L stock solution, which was stored at 4 °C.

In order to determine the optimal alum dose, a range of alum doses were added to 250 mL glass beakers holding 150 mL spiked test water at room temperature being stirred at 25 rpm. After alum dosing, the water was mixed rapidly at 100 rpm for 2 minutes, mixed slowly at 25 rpm for 30 minutes, and allowed to settle for 60 minutes. Turbidity and pH of the supernatants were measured immediately using a 2100N turbidimeter (HACH, Loveland, CO) and a AR20 pH/conductivity meter (Fisher Scientific), respectively. Supernatants were stored in polypropylene centrifuge tubes at 4 °C until TOC and ICP-MS analysis. Jar tests were conducted in triplicate for each NP in each water type.

The optimal alum dose was determined as the minimum dose required to effectively remove both turbidity and TOC; this method is similar to that employed in full-scale drinking water treatment. If the optimal dose for the turbidity and TOC were not the same, the higher dose between the two was selected. Jar tests were also conducted to determine the optimal alum dose for SFW_NOM without NPs (n=3) for comparison to the optimal alum dose in SFW_NOM containing NPs.

Membrane filtration. Concurrently with the jar test experiments, two membrane filtration experiments were conducted using the same batch of test water. Aliquots of 1 mg/L NPs in experimental waters were filtered through a polyvinyldine fluoride (PVDF) flat-sheet membrane (Millipore, Millex) with a nominal pore size of 0.45 μm for microfiltration (MF) or a ceramic flat-sheet membrane (Whatman, Anotop 25) with a nominal pore size of 0.02 μm for ultrafiltration (UF).

Ultra-pure water was pumped through the membranes at 1mL/min until a stable UV signal was reached. Spiked test waters were then pumped through the membranes at 1 mL/min for 120 minutes. The UV absorbance was monitored throughout at 254 nm, 320 nm, and 370 nm for Ag,

TiO$_2$, and ZnO NPs respectively, which was determined by UV spectral scans. A composite sample, consisting of 15 seconds of filtrate collection at 1, 5, 30, 60, 90, and 120 minutes, was collected for ICP-MS analyses. Samples were stored at 4°C until analysis. Each water type, without NPs, was filtered through MF and UF and a composite filtrate sample was analyzed by ICP-MS and used to background correct the results of spiked water experiments. Experiments were conducted in triplicate for each NP in each water type.

Statistical analyses. Statistical analyses were conducted using SigmaPlot 11 and STATA 11. Comparison of two means were conducted using a student's t-test. Comparison of multiple means were conducted using one-way analysis of variance. The Holm-Sidak method, Dunn's one way analysis of variance on rank, or the Tukey Test were used to determine significance among multiple pair-wise comparisons.

Results

Nanoparticle removal by alum coagulation. The optimum alum dose, defined as the minimum alum dose achieving the lowest turbidity or TOC measurement, was determined for each NP and test water combination (Table 2). The optimal doses determined by turbidity or TOC removal were not significantly different for each experimental condition (test water and NP). Alum doses within test waters differed by NP in SFW ZnO NPs vs both TiO$_2$ and Ag NPs ($p < 0.05$) and in WWeff ZnO vs. Ag NPs ($p < 0.01$) (Table 2). All of the optimum alum doses met the goals for percent NOM removal according to the Enhanced Coagulation Rule (See Supplemental Material, Table S1), which sets guidelines for percent NOM removal based on the initial TOC and alkalinity (EPA 1999).

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The optimum alum dose for SFW_NOM without NPs, based on turbidity removal, was $3.13 \pm$ 0.3 mg Al/L (See Supplemental Material, Figure S2). This dose was not statistically different than the optimum dose for SFW_NOM containing any type of NPs (Table 2, See Supplemental Material, Figure S2).

The supernatant of the optimal dose was analyzed for total metals by ICP-MS and NP breakthrough was estimated (Figure 1). Breakthrough of NPs was lowest for Ag and TiO_2, with less than 20% and 10% breakthrough for all waters, respectively. ZnO had the highest breakthrough, with over 60% in most waters and complete breakthrough observed in SFW (Figure 1). Within each NP type, there was no statistically significant difference in breakthrough by water source. Within each water source, ZnO breakthrough was statistically different from both Ag and TiO_2 at $p<0.05$ (Figure 1). Breakthrough was confirmed as metals were detected in most finished water samples, ranging from 0-305 µg/L Ag, 0-297 µg/L Ti, and 340-3200 µg/L Zn (Supplemental Material, Table S4 'Coagulation/ Flocculation/ Sedimentation').

Removal by membrane filtration. The composite MF and UF samples were analyzed by UV absorbance and ICP-MS to estimate NP removal (Figure 2). The UV absorbance was measured throughout the membrane removal experiments and a greater UV absorbance indicates that more NPs were passing through the membrane into the filtered water. The UV absorbance results were similar for all NPs in all waters, with greater UV absorbance in the MF permeate than the UF (Supplemental Material, Figure S3). However, the UV signals from both MF and UF were low and not statistically different than the test water without any NPs, indicating a low breakthrough of NPs through the membranes. The results from ICP-MS indicate that NP breakthrough through MF varied by both NP type and water source. After MF, Ag, Ti, and Zn were detected up to 743,

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1330, and 2261 µg/L, respectively. After UF, Ag, Ti, and Zn NPs were detected up to 44, 158, and 3202 µg/L, respectively (Supplemental Material, Table S4).

Overall, there was less breakthrough following UF than MF (Figure 2). UF resulted in less than 5% breakthrough for Ag and TiO_2 from all waters and ZnO from GW (see Supplemental Material, Table S5). Breakthrough of Ag NPs from all waters except GW and TiO_2 NPs from all waters except SFW_NOM through MF was less than 20%. However, ZnO breakthroughs were significantly higher than Ag and TiO_2 NPs in both MF and UF in all waters (see Supplemental Material, Table S5).

Discussion

Nanoparticle breakthrough during conventional treatment. Nanoparticles can be removed through coagulation if they are enmeshed by the coagulate floc as it sediments out of the water, in a process called sweep floc (Crittenden et al. 2005). Alternatively, coagulants added to the water may impact NP stability by producing positively charged hydrolytic species that neutralize negative surface charges on NPs (Westerhoff et al. 2008), resulting in greater NP aggregation since electrostatic repulsion is mitigated (Petosa et al. 2010).

A key operational parameter for coagulation is coagulant dose. For conventional treatment, water characteristics drive the optimal coagulant dose (O'Melia et al. 1999; Shin et al. 2008). Optimal doses for GW, SW, and SFW_NOM were similar in this study regardless of the NP type (Table 2) and the optimal alum dose was not statistically significantly different for SFW_NOM with or without NPs (Table 2 and Supplemental Material, Figure S2). These results confirm that NOM was the main driver for optimal coagulant doses and not the addition of the NPs to the water

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(even at a high particle concentration of 1 mg/L). In our experiments, due to the relative abundance of NOM to NPs, hydrolytic aluminum species formed from potassium alum will preferentially react with the free NOM (Hyung and Kim 2009; O'Melia et al. 1999), instead of NPs in water.

Practically, the low expected environmental concentrations of NPs in surface waters are even less likely to affect the optimal coagulant dose in water treatment plants. The optimal alum dose for drinking water treatment is typically determined by evaluating removal of turbidity or TOC following jar tests (Crittenden et al. 2005; EPA 1999). In our experiments, use of traditional measurement techniques to determine optimal dose resulted in finished waters that met the EPA coagulation guidelines (EPA 1999). However, the optimal coagulant dose for TOC removal, as required by the EPA guidelines, was not sufficient for removal of the NPs as there were detectable levels of Ag, Ti, and Zn in all the finished waters above those detected in the test water without NPs(See Supplemental Material, Table S3). These metals may be NPs, ions released from NP surfaces, or fully dissolved NPs. Increased metal concentrations in finished waters, whether NP or ions, is a concern for human health and for water treatment.

Nanoparticle breakthrough during membrane filtration. Filtration by LPM has become increasingly used for drinking water treatment and potable water reuse (Guo et al. 2010; Huang et al. 2009). In this study, MF was assessed with a 0.45 μm PVDF membrane, which is at the upper pore size limit of membranes employed by full-scale membrane filtration plants (Van Der Bruggen et al. 2003). We investigated UF using a 0.02 μm ceramic membrane, which was smaller than the NP primary particle size and had pore sizes that were uniformly 20 nm (Van Der Bruggen et al. 2003).

Removal of compounds and contaminants by LPM filtration is predominantly based on physical sieving effects (Crittenden et al. 2005; Westerhoff et al. 2008). Therefore, removal of NPs by membrane filtration depends on membrane pore size, NP size, and NP stability – either aggregation or dissolution. We outlined three potential outcomes for NPs in source water used for drinking water treatment: NPs aggregating with other NPs or NOM in the water, NPs remaining as primary particles, or NPs dissolving into ions (Figure 3). In experimental waters with NOM (all except SFW), the NPs aggregated to sizes ranging from 199-421 nm, 248-1147 nm, and 292-353 nm for Ag, TiO_2, and ZnO NPs respectively (Table 1). The extent of aggregation was influenced by the characteristics of the experimental waters (Table 1). Most aggregates will be larger than the membrane pore sizes utilized by LPM filtration and thus will not pass into finished drinking water. Our results confirm that MF was most effective for larger NP aggregates. Small NP aggregates or stabilized NPs, such as Ag and TiO_2 NPs in GW and SFW_NOM (Table 1), could break through the membrane.

Investigation into NP dissolution was facilitated by UF, since the pore size was smaller than the primary particles. Therefore, any metals detected in the UF filtrate should be ions. UF has been used by other researchers to distinguish soluble species of metals (Ussher et al. 2010). At the pH and ZnO NP concentration of most of the experiments, Zn(II) was the predominant species, indicating ZnO NP dissolution into zinc ions (Stumm and Morgan 1996). Dissolution of ZnO NPs was confirmed by similar NP removals between MF and UF, since only dissolved ions could break through UF (Figure 3) and since UF removal of ZnO NPs was greatest from the GW source water, which had the highest initial pH. However, ZnO NP dissolution was incomplete, since there was some ZnO removal in all waters with MF and some ZnO NP aggregates measured by DLS (Table 1).

Consistent removal of stabilized NPs will only occur if membrane pore sizes are smaller than NPs, such as the UF membrane tested in these experiments. However, dissolved ions released by ZnO NPs passed through UF membranes and would require filtration with even tighter membranes or the use of other treatment technologies not commonly used in large-scale drinking water treatment, such as ion exchange. For potable water reuse, reverse osmosis has frequently been used after LPM filtration or conventional treatment, and should serve as an effective barrier for dissolved metal ions.

Implications for drinking water treatment and public health. As NPs in production and the environment increase, it is important to understand human exposures to NPs, especially as the literature on the adverse effects of NPs increases. Drinking water treatment provides a barrier to contaminant exposure via the ingestion of drinking water. However, this research indicated NP breakthrough into finished water after coagulation/flocculation/sedimentation as well as membrane filtration. Although experimental conditions were higher than expected environmental concentrations, the removal efficiencies are not expected to change significantly with changing concentration.

As illustrated in Figure 3, NP aggregate size is an important parameter for NP removal. Larger aggregates will be removed by settling floc during conventional treatment and by physical separation during advanced membrane filtration.

Investigation into NP size in source waters can inform the choice of treatment technology, including membrane pore size. Enhanced NP removal by LPM filtration must be balanced with increased energy costs and greater membrane fouling that is likely to occur when NOM is

present in source water. Moving forward, it may be necessary to combine treatments in sequence for optimum removal of NPs (Moon et al. 2009; Zhang et al. 2008).

Our research indicated that use of traditional drinking water quality parameters, such as TOC and turbidity removal, resulted in finished water that met EPA guidelines for coagulation but contained detectable metals (Supplemental Material, Table S5). More sensitive detection methods and instrumentation, such as ICP-MS, were necessary to accurately determine NP removal and measure residual metals in finished waters. These new methods are more expensive and time consuming and thus may be impractical for water utilities to use to continuously monitor finished water quality. New simpler, on-line detection methods for NPs in water will be necessary to protect public health by monitoring NP removal during drinking water treatment.

Although the health effects of ingesting NPs, especially at low concentrations, are unknown, it is important to apply the precautionary principle and begin to consider NPs as emerging drinking water contaminants. The concentrations detected in finished waters in these experiments were below the concentrations found to damage intestinal cells *in vitro* (Abbott Chalew and Schwab 2013; Koeneman et al. 2010) but high enough to cause adverse effects to aquatic organisms (Bowman et al. 2012; Gaiser et al. 2012). However, NPs and metal ions released from NPs will only increase over time with greater production and use of NP-containing consumer products leading to a potentially greater health risk. Despite high removals from conventional and advanced treatment, our experiments detected metals, possibly NPs, in finished waters. Until the health effects of NP the ingestion are better understood, it is necessary to determine appropriate removal processes for both the NPs and the released ions so that water continues to protect public health into the future.

Conclusions

As NP containing products increase, there is greater likelihood that NPs will contaminate drinking water resources. Using NPs spiked into synthetic and natural waters, NP breakthrough was estimated from conventional and advanced drinking water treatment. Simulated conventional treatment resulted in 10-20% NP breakthrough. Membrane filtration, especially UF, was more effective than conventional treatment for NP removal. Despite high removals, finished waters contained detectable metal concentrations, which may pose hazards to human health. NP removal, by both treatment processes, was affected by NP stability including aggregation and dissolution. When NPs dissolve, such as observed with ZnO NPs, it may be necessary to employ other treatment processes. NPs should be considered as an emerging drinking water contaminant and their removal during drinking water treatment should be monitored to protect public health.

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Table 1. NP characterization in test waters. NP size was measured using dynamic light scattering (n=3 samples with 4 measures for each water type) (average ± standard deviation).

Water type	Ag NPs (nm)	TiO$_2$ NPs (nm)	ZnO NPs (nm)
Groundwater	223.4 ± 81.1	271.6 ± 16.6	292.6 ± 16.8
Surface Water	390.3 ± 90.5	1147 ± 234	353.6 ± 50.1
Synthetic Freshwater	248.1 ± 68.4	3338 ± 984	7021 ± 5066
Synthetic Freshwater with NOM	199.0 ± 38.6	248.1 ± 8.03	321.1 ± 89.0
Tertiary Wastewater Effluent	421.3 ± 82.3	751.3 ± 102	354.8 ± 50.9

Table 2. Optimal alum dose (mg Al/L) for each NP type as determined by turbidity and total organic carbon (TOC) removal in mg C/L (n=3 experiments for each NP in each water type) (average ± standard deviation).

Water type	Ag NPs Turbidity	Ag NPs TOC	TiO$_2$ NPs Turbidity	TiO$_2$ NPs TOC	ZnO NPs Turbidity	ZnO NPs TOC
Groundwater	4.36 ± 0.33	3.98 ± 1.14	4.55 ± 0.57	3.55 ± 0.28	3.98 ± 0.57	3.22 ± 1.19
Surface Water	3.41 ± 0.57	3.79 ± 0.85	3.22 ± 0.33	3.27 ± 0.55	2.75 ± 0.17	2.84 ± 0.57
Synthetic Freshwater	2.62 ± 0.42	2.84 ± 0.52	2.66 ± 0.68	2.78 ± 0.97	1.21 ± 0.14[*]	1.42± 0.57[*]
Synthetic Freshwater with NOM	3.32 ± 0.16	3.70 ± 0.74	3.05 ± 0.22	3.41 ± 1.54	3.36 ± 0.37	3.84 ± 0.55
Wastewater Effluent	10.2 ± 0.97[**]	10.64 ± 1.31[**]	9.40 ± 0.33	9.95 ± 1.42	8.36 ± 0.33[**]	9.10 ± 0.57[**]

[*]Statistical difference from other NPs at $p < 0.05$

[**] Statistical difference from other NPs at $p < 0.01$

Figure Legends

Figure 1. Mean NP breakthrough through simulated conventional treatment determined by ICP-MS (n=3, standard deviation). Residual a) Ag, b) Ti, and c) Zn in groundwater (GW), suburban stream (SW), synthetic freshwater (SFW), SFW with NOM (SFW_NOM), and tertiary wastewater effluent (WWeff). Reference line indicates no removal.

Figure 2. Mean NP breakthrough through advanced treatment as determined by ICP-MS (n=3, standard deviation). Residual a) Ag, b) Ti, and c) Zn in finished waters after microfiltration (black bars) and ultrafiltration (gray bars) of groundwater (GW), suburban stream (SW), synthetic freshwater (SFW), SFW with NOM (SFW_NOM), and tertiary wastewater effluent (WWeff). Reference line indicates 100% breakthrough. * indicates differences between waters within the NP type ($p < 0.05$), ** indicates Zn residuals differ from both Ag and Ti at $p < 0.05$ and *** $p < 0.01$.

Figure 3. Mechanisms of NP stability and removal by membrane filtration. The NP can: 1) aggregate, 2) remain as a single NP, or 3) dissolve into ions. Stable NPs (2) or ions (3) would pass through microfiltration, but not aggregates (1). Only ions (3) would pass through the ultrafiltration membrane. Diagram not to scale.
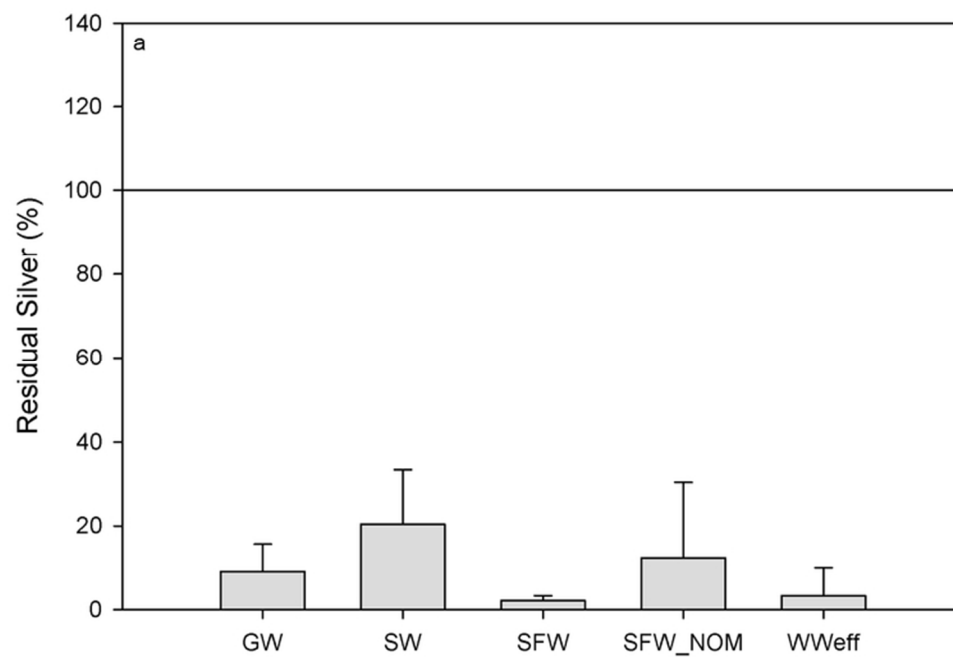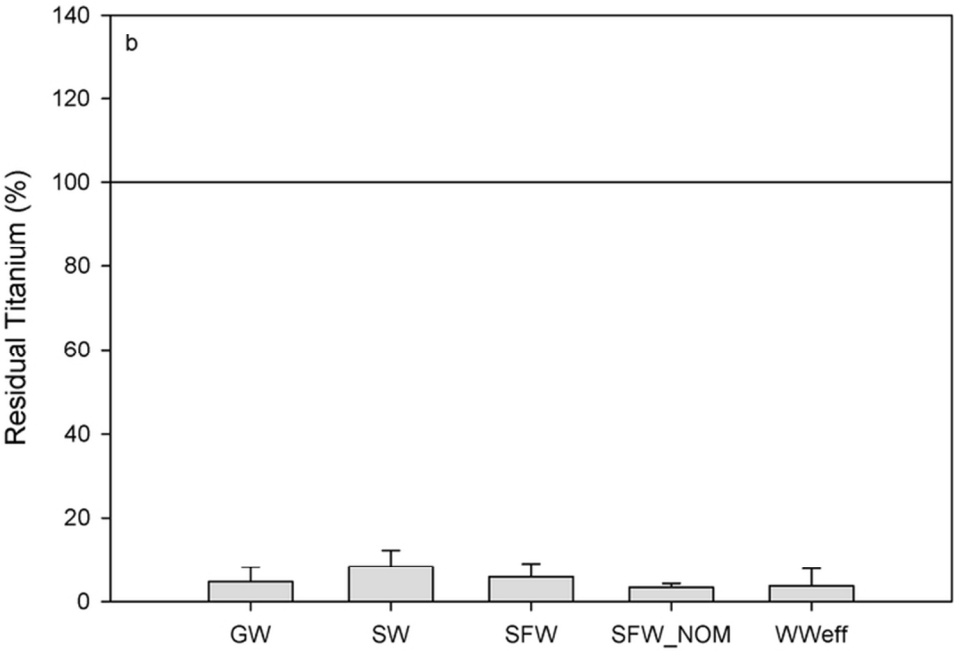
Figure 1a
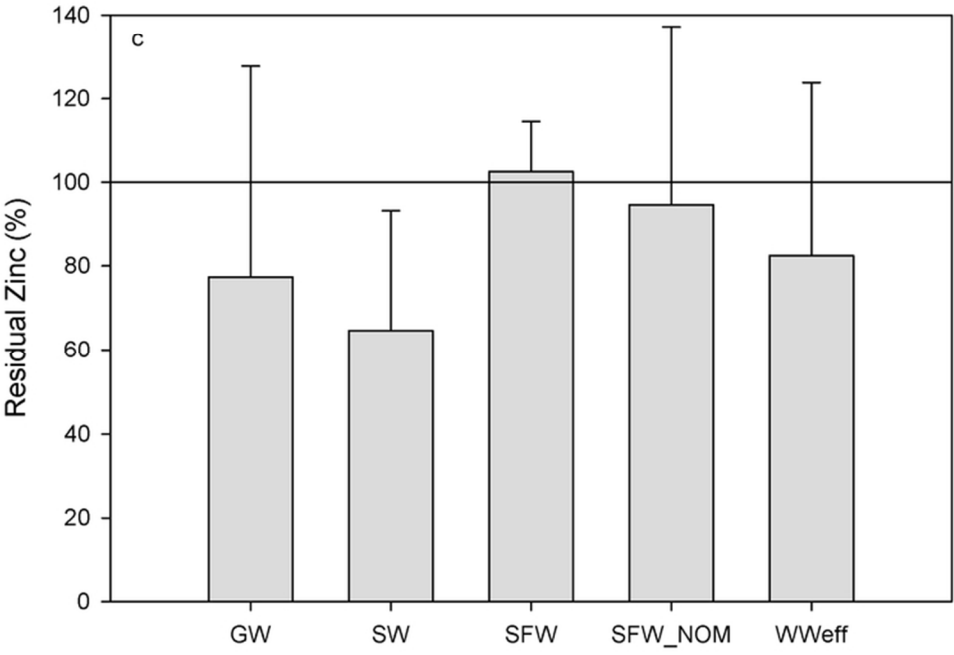66x49mm (300 x 300 DPI)

Figure 1b
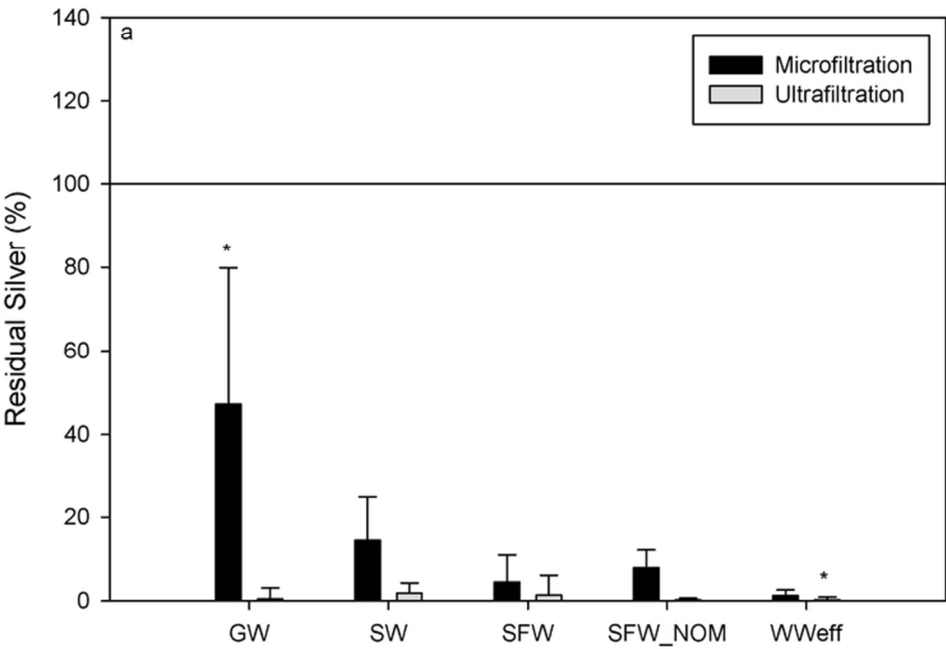66x49mm (300 x 300 DPI)

Figure 1c
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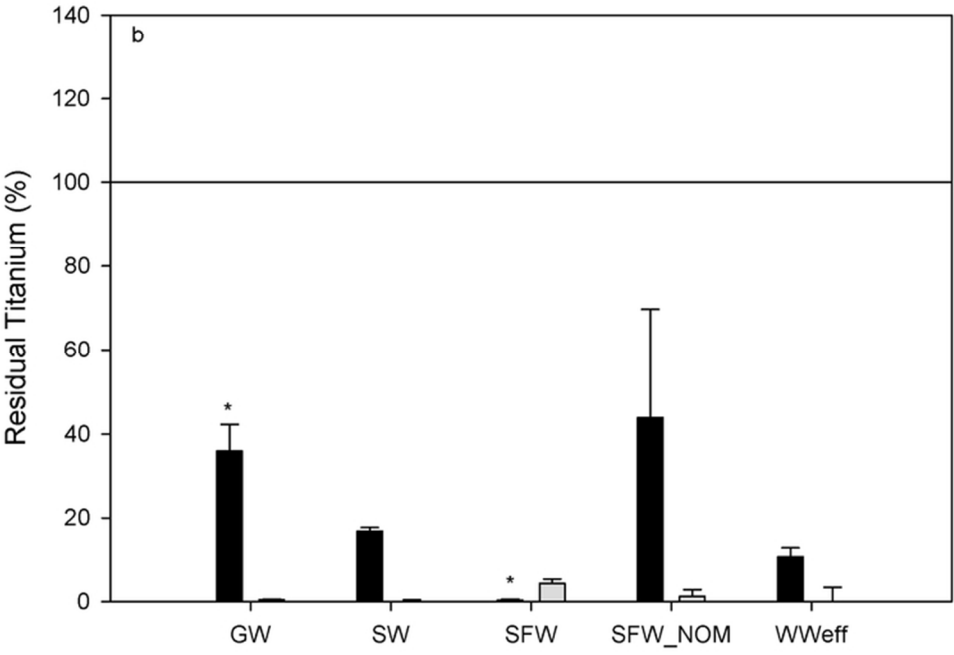
Figure 2a
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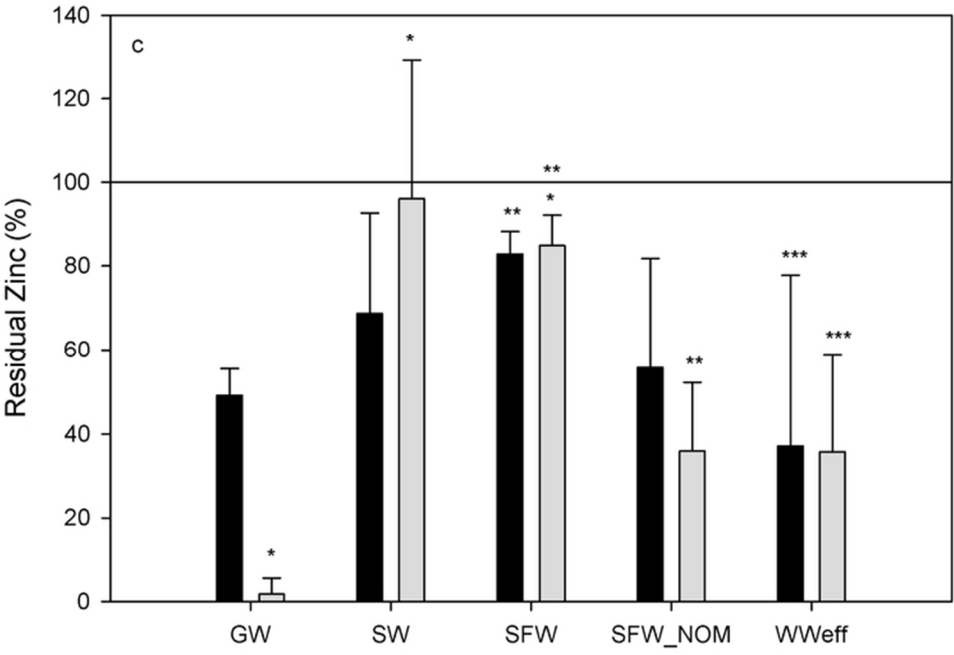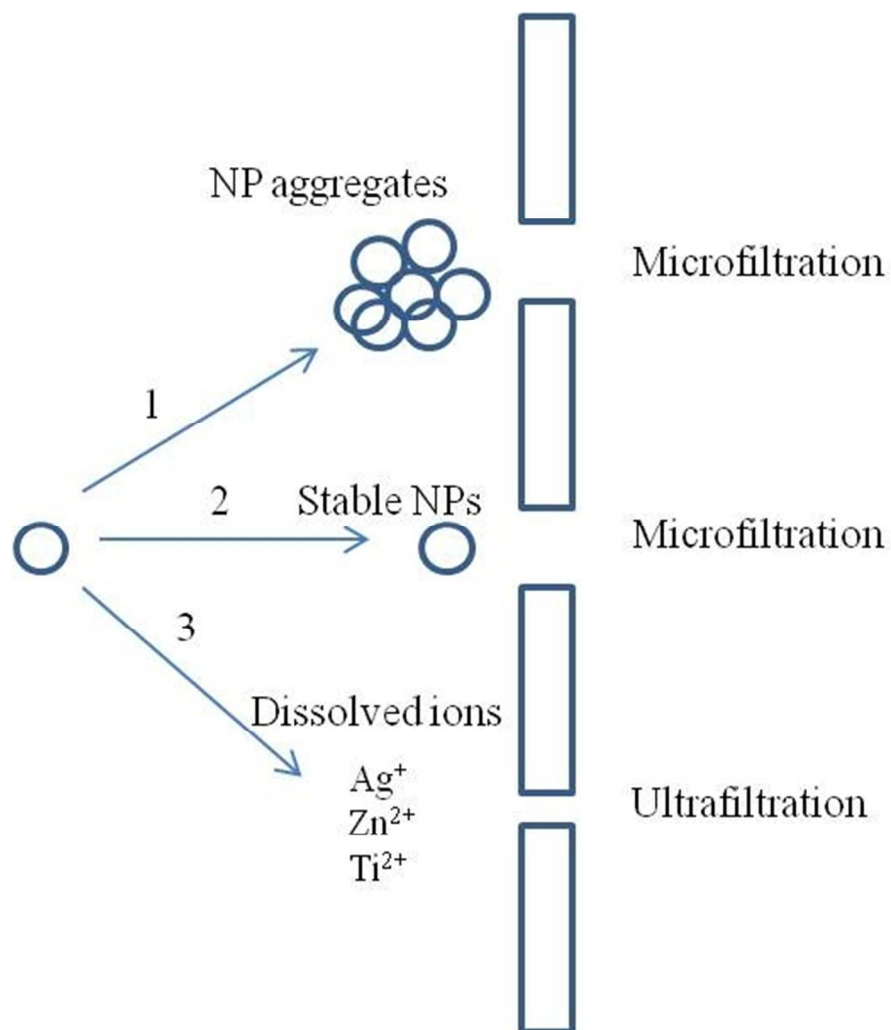
Figure 2b
66x49mm (300 x 300 DPI)

Figure 2c
66x49mm (300 x 300 DPI)

Figure 3
100x102mm (150 x 150 DPI)